VI.A.3 Discovery of Novel Complex Metal Hydrides for Hydrogen Storage through Molecular Modeling and Combinatorial Methods

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Objectives

Discovery of complex metal hydrides through molecular modeling and combinatorial methods which will enable a hydrogen storage system that meets DOE 2010 performance goals. The deliverables include:

- Delivery of one kilogram of optimized material
- Development of a potential manufacturing process
- A design for a hydrogen storage system
- Accompanying documentation

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Cost
- B. Weight and Volume
- D. Durability
- E. Refueling Time
- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption.

Technical Targets

This project uses virtual high-throughput screening by computer modeling and combinatorial experimentation to identify promising metal hydrides for vehicular on-board hydrogen storage applications meeting DOE 2010 system targets:

- Useable specific energy from H_2: 2 kWh/kg
- Useable energy density from H_2: 1.5 kWh/L
- Storage system cost: 4 $/kWh
- Cycle life: 1,000 Cycles
- Minimum and maximum delivery temperature: -30/85 °C
- System fill time: 3 minutes for a 5-kg hydrogen system

Table 1. On-Board Hydrogen Storage System Status
(**Data is based on material only, not system value)

Storage Parameter	Units	2010 System Target	FY05 materials**
Specific Energy	kWh/kg (wt. % H_2)	2.0 (6 wt.%)	1.5 (4.4 wt%)
Volumetric Energy Capacity)	kWh/L	1.5	1.1

** Values measured in our lab for 2%Ti-$(OiPr)_4$/$NaAlH_4$, for second-cycle H_2 desorption from 80°C /1 bar to 235°C/16 bar, using a powder density of 0.724 kg/L.

Approach

Identify H_2 storage material enabling DOE 2010 targets and increase understanding of promoted complex hydrides using:

- Virtual high-throughput screening of new materials and catalysts
- Combinatorial synthesis and testing
- Calculation of thermodynamics from first-principles
- Extensive testing, characterization and modeling of leads

Demonstrate viability for commercial application:

- Scale-up material meeting targets to 1-kg for samples for independent testing by Southwest Research Institute
- Identify potential commercial manufacturing route
- Design H_2 storage system
- Perform material manufacturing cost estimates

FY05 Accomplishments

- Developed a simulated annealing procedure to estimate crystal structures of mixtures of complex hydrides.
- Demonstrated virtual high-throughput screening of complex hydrides at a rate of 1,000 phases per month using empirical force-fields and simulated annealing.
- Developed a database of first-principles calculated physical properties of 28 known crystalline metal hydrides and calculated hydriding enthalpies for them.

- Using medium-throughput combinatorial experimentation (8 experiments per run) screened the Na-Li-Mg/AlH_4 phase diagram using three different preparation methods at 21 samples/each. No improved hydride was found compared to Ti-doped $NaAlH_4$.
- Began expansion of the mixed alanate investigation to other elements.
- Construction of the high-throughput H_2 storage assay has been completed and it is currently being installed at UOP.

Future Directions

- Complete the evaluation of mixtures of $LiAlH_4$, $NaAlH_4$, $KAlH_4$, $Be(AlH_4)_2$, $Mg(AlH_4)_2$ and $Ca(AlH_4)_2$ using virtual high-throughput screening and combinatorial experimentation.
- Extend the virtual high-throughput screening and combinatorial experimentation to mixtures of borohydrides, alanates and amides.
- Further refine first-principles computational methods for predicting structures and compositions of complex hydrides and apply them to new multi-component hydride systems.
- Shake down and validate the high-throughput synthesis and testing systems and apply them to the combinatorial experimentation.
- Evaluate alternate dopants using high-throughput combinatorial experimentation in systems not limited by thermodynamic reversibility as indicated by modeling.

Introduction

Metal hydrides have the potential for reversible on-board hydrogen storage with hydrogen release at low temperatures and pressures. However, known hydrides are either too heavy (such as $LaNi_5H_6$), or require high temperature to release hydrogen (such as MgH_2). It has been shown that Ti-doped complex hydride $NaAlH_4$ can reversibly absorb hydrogen at lower pressure and temperature than MgH_2 and has a higher gravimetric capacity and lower cost than $LaNi_5H_6$. This project will systematically survey complex hydrides to discover a material which would enable a hydrogen storage system that meets DOE's 2010 goals.

Approach

The team will apply combinatorial experimentation and molecular modeling to discover materials with optimum thermodynamics and kinetics for on-board hydrogen storage. Virtual high-throughput screening (VHTS) exploits the capability of molecular modeling to estimate the thermodynamics on the computer more quickly than can be measured in the laboratory. VHTS will be used to focus the synthesis effort on making the most promising materials. First-principles calculations will be used to determine thermodynamic properties of these new materials. Even more importantly, the coupling of combinatorial experiments with molecular modeling of structural and thermodynamic properties will provide insights into the underlying mechanisms of action in these complex materials, permitting the design of hydrogen storage materials which would never have been envisioned otherwise.

Results

Synthesis

Synthesis efforts focused on the Na-Li-Mg/AlH_4 phase diagram. Early experiments to prepare Ti-doped $Mg(AlH_4)_2$ indicated extensive decomposition during ball milling. A detailed safety review identified several potential hazards: explosion inside the mill in case of a H_2 release, as well as mechanical and fire hazards during unclamping of the milling vial due to pressure build-up and release of H_2 or sample. Equipment and procedural modifications were made to address these issues. Ti-doped $LiAlH_4$ also decomposed during milling, showing only Li_3AlH_6 via x-ray diffraction (XRD) afterwards. Ti-doped $NaAlH_4$ only showed minor decomposition to Na_3AlH_6 during milling.

Because of concern that decomposition during milling would prevent the formation of mixed

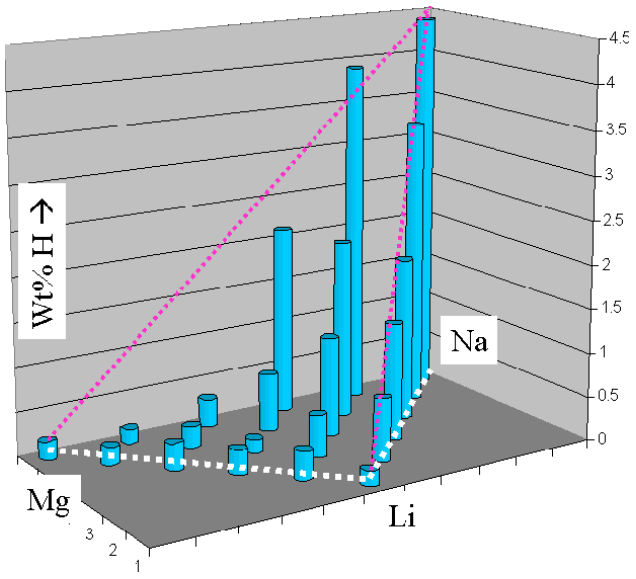

Figure 1. Reversible H_2 Content for the Na-Li-Mg/AlH_4 Phase Diagram

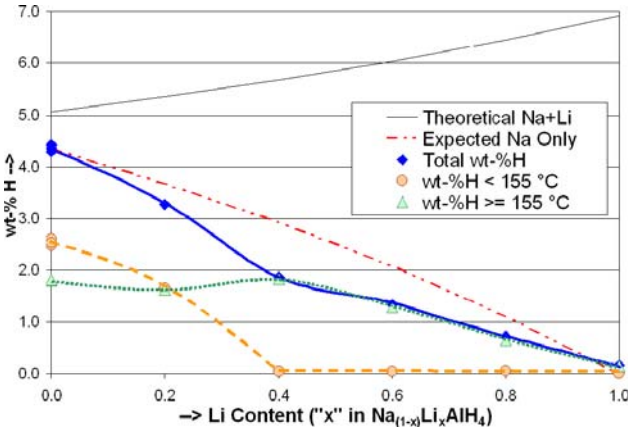

Figure 2. Reversible H_2 Content for Na-Li/AlH_4 Binary Mixtures (Solid line calculated assuming that both Na and Li are fully reversible; dashed line calculated assuming that only Na contributes, with actual reversibility; symbols show total wt-% H, wt-%H desorbing < 155°C, and wt-%H desorbing >= 155°C.)

Na-Li-Mg alanate phases, a modified milling procedure was developed to improve interaction between the alanates while reducing decomposition due to the dopant. Both approaches were used for the entire Li-Na-Mg/AlH_4 phase diagram. XRD characterization of each of the milled materials showed no new phases. Because of the importance of reversibility of these systems, the reverse reaction was also studied. In this case, samples were prepared from nano activated aluminum (100-nm) and the simple hydrides LiH, NaH, MgH_2, KH and CaH_2. Titanium isopropoxide was also doped into these samples. On the informatics side, database tables and data-entry tools for the synthesis materials and unit operations have been developed and are currently being implemented in the UOP Combi database.

Test Results

The 8-reactor medium-throughput system has been validated against published results and is fully operational. The standard test protocol consists of the following sequence: (a) a first thermal desorption to measure the H_2 content of the as-synthesized samples; (b) H_2 treatment at 125°C at 87 bar for 12 hours to re-hydride the samples, (c) a second thermal desorption to measure the reversible H_2 content.

Figure 1 shows the reversible H_2 content as a function of alanate composition for the Na-Li-Mg/AlH_4 phase diagram samples made using standard milling. The modified procedure gave less decomposition during milling but the second cycle results are essentially the same as with the standard milling. These results show that reversible H_2 content decreases as Na is replaced by Li and/or Mg.

Figure 2 shows the reversible H_2 content for Na-Li/AlH_4 binary mixtures in more detail. The solid line shows the theoretical H_2 content assuming that both Na and Li fully contribute to reversible alanate formation, reflecting the potential for an improved material. The dashed line shows the calculated H_2 content assuming that only Na contributes to reversible alanate formation, further taking into account the finite reversibility of $NaAlH_4$. The observed results are below the dashed line indicating that Na-Li/AlH_4 mixtures with enhanced H_2 content do not form. Separation of the data into H_2 desorbing below or above 155°C indicates that the low-temperature AlH_4-like H_2 is inhibited by Li, vanishing near 40 atom-%Li. Much of this low-temperature H_2 is converted into a high-temperature AlH_6-like H_2. This is supported by the observation in XRD of the formation of the Na_2LiAlH_6.

Figure 3 shows the reversible H_2 content for the Na-Mg/AlH_4 binary mixtures in more detail. The solid and dashed lines have been calculated as were

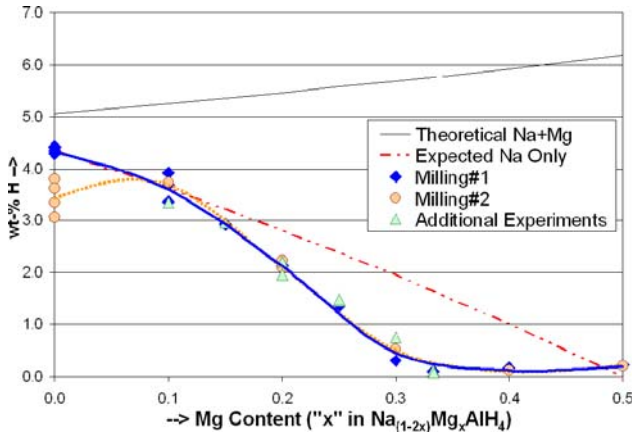

Figure 3. Reversible H_2 Content for Na-Mg/AlH_4 Binary Mixtures (Solid and dashed lines calculated as in Figure 2, symbols show experimental data.)

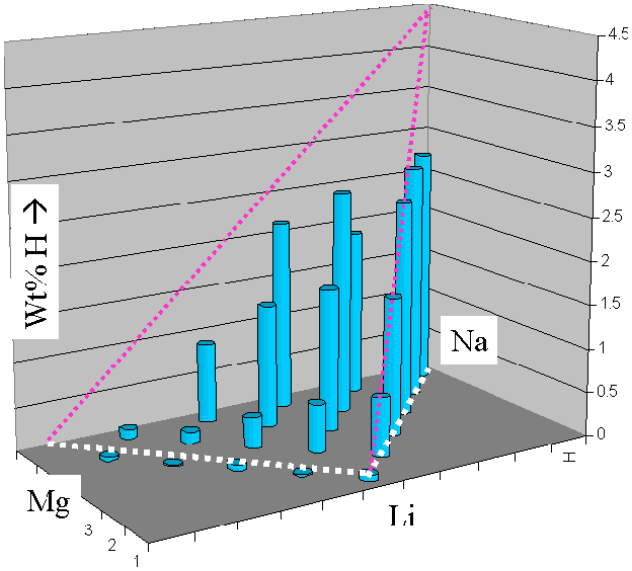

Figure 4. Reversible H_2 Content for Na-Li-Mg/AlH_4 Phase Diagram Samples made from Simple Hydrides and Al

done in Figure 2. The observed results are below the dashed line indicating that Na-Mg/AlH_4 mixtures with enhanced H_2 content do not form. In fact, the reversible H_2 content declines more rapidly than the dashed line, reaching zero at a composition of $Na_{0.33}Mg_{0.33}$. At this point XRD of the used samples shows primarily Al and $NaMgH_3$, which is not reversible at our conditions.

Figure 4 shows the results for samples made using the reverse reaction, with a hydriding step

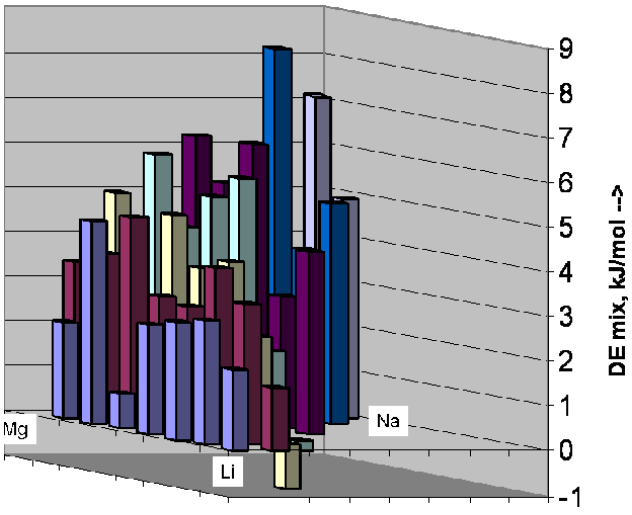

Figure 5. Mixing Energies for the Na-Li-Mg/AlH_4 Phase Diagram Calculated by Molecular Mechanics

before the first desorption. The pure Na point is somewhat low, otherwise these results are consistent with the alanate results i.e., Li and Mg reduce reversible H_2 content. We have begun experiments expanding the alanate compositional space beyond Na-Li-Mg/AlH_4 by including K and Ca but these experiments are not yet complete. Regarding the informatics, tools to automatically process the medium throughput test data and characterize desorption curves have been developed and are currently being implemented.

VHTS of Complex Hydrides

We have developed a simulated annealing approach to estimate the crystal structure of complex hydrides. This approach predicts crystal structures which are less than 0.1 eV/H_2 above the energy of the lowest energy crystal structure. This level of accuracy is enough to determine whether a mixed alanate phase is stable. Our simulated annealing approach and the empirical force-field developed last year is well suited to estimating the heats of mixing of complex hydrides and the VHTS of complex hydrides. The current methods can estimate the heats of mixing for approximately 1,000 phases per month. The heats of mixing from VHTS and heats of formation of pure phases from experiment and first-principles modeling can be used to predict the stability of a mixed phase. VHTS has been applied to mixtures of $LiAlH_4$, $NaAlH_4$ and $MgAlH_4$ as shown in Figure 5, but no mixtures of these alanates

were predicted to be stable. This is in agreement with the experimental results from this project and the literature.

First-Principles Modeling

We have created a database of first-principles calculations of structural and thermodynamic properties for 28 complex hydrides with known crystal structures. This database will be used to develop combinatorial descriptors, such as reaction enthalpies Delta-H^o, metal-hydrogen bond lengths, cation-cation distances, H-M-H bond angles, electronic band gaps, etc. The crystal structures of these compounds are being used to predict the physical properties of new multi-component hydrides with yet-unknown crystal structures. In addition, a heuristic model of electrostatic energetics of complex hydrides has been tested on the Na-Mg/AlH_4 system. However, subsequent first-principles calculations showed that their formation enthalpies are actually positive indicating that these compounds will not form, in accordance with our experimental data (the points at $Na_{0.5}Mg_{0.25}$ and $Na_{0.33}Mg_{0.33}$ in Figure 3). Therefore, it was concluded that ionic size effects need to be included in the heuristic model.

High-throughput Combinatorial Capability

A high-throughput parallel-milling process (48 samples per experiment) has been demonstrated successfully in a proof-of-principle experiment using the Ti/$NaAlH_4$ standard material. A high-throughput synthesis instrument for powder and liquid dosing in an air-free environment will be purchased commercially. Construction of the high-throughput test system has been completed and it is being installed at UOP.

Conclusions

The experimental medium-throughput synthesis and testing, and VHTS methodologies have been developed and validated. Application to mixtures of $LiAlH_4$, $NaAlH_4$ and $Mg(AlH_4)_2$ did not reveal any mixture with improved properties for hydrogen storage over $NaAlH_4$. The methodologies are currently being applied to mixtures of borohydrides, alanates and amides. The high-throughput screening system is in place and undergoing shakedown, the high-throughput synthesis capability will be completed by 4Q05. A database of first-principles calculated physical properties of 28 known crystalline metal hydrides has been calculated, together with hydriding enthalpies of these compounds.

FY 2005 Publications/Presentations

1. "Discovery of Novel Complex Metal Hydrides for Hydrogen Storage Through Molecular Modeling and Combinatorial Methods," presentation to the H_2 Storage Tech Team Meeting, 1/20/2004, Detroit, MI by Gregory J. Lewis.
2. "Discovery of Novel Complex Metal Hydrides for Hydrogen Storage Through Molecular Modeling and Combinatorial Methods," presentation to the 2005 Hydrogen Program Annual Review, May 25, 2005, Crystal City, VA, by J.W. Adriaan Sachtler.
3. "Discovery of Novel Complex Metal Hydrides for Hydrogen Storage Through Molecular Modeling and Combinatorial Methods," poster at the IPHE International Hydrogen Storage Technology Conference, June 19 - 22, 2005, Lucca, by J.W. Adriaan Sachtler, Gregory J. Lewis, John J. Low, David A. Lesch, Paul M. Dosek, Syed A. Faheem, Yune D.T. Le, Craig M. Jensen, Vidvuds Ozolins, Blanka Magyari-Kope, and C. Wolverton.